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Hydrodeoxygenation of the Aqueous Fraction of Bio-oil with Ru/C and Pt/C catalysts

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Abstract

In this paper we discuss the continuous flow hydrogenation of the water soluble fraction of bio-oil (WSBO) with Ru/C and Pt/C catalysts. Temperatures higher than 125°C lead to homogeneous reactions within the aqueous phase of bio-oil. Low temperature hydrogenation (LTH) at 125°C over Ru/C catalyst and with WHSV of 1.5-3 hr⁻¹ was required to stabilize the bio-oil so higher temperature hydrogenation (HTH) could occur. The main products from LTH were ethylene and propylene glycols and sorbitol. At these temperatures only small amounts of acetic acid (AA), levoglucosan, furanone, phenol and phenol substitutes were hydrogenated. In the HTH step, the sorbitol was hydrogenated to mono-alcohols and diols by hydrogenolysis and secondary hydrogenation reactions. Up to 45% carbon in WSBO was converted to useful products (gasoline-cuts and diols) in the HTH step over Pt/C catalyst at 250°C and WHSV of 3 hr⁻¹. The reactions product distribution can be controlled by modifying operating pressure and temperature. The production of gasoline range compounds (C4-C6 alkanes and C1-C6 alcohols) is favoured at low pressure (750 psi). Increasing the reaction pressure decreased the amount of carbon that was converted into gas phase products.

Keywords: bio-oil upgrading, hydro-treating, aqueous phase processing, bio-gasoline, bio-chemicals.

1.0 Introduction

Pyrolysis is a promising technology for conversion of biomass into liquid fuels mainly due to its low capital and operating cost advantages compared to competing technologies such as fermentation and gasification [1-6]. The liquid fuel produced by pyrolysis is called bio-oil or pyrolysis oil. The pyrolysis oil has half the energy content of a petroleum based liquid fuel, a high oxygen content (45-50 wt%), low pH and a complex composition. In addition the pyrolysis

oil is unstable and undergoes phase separation with time [7,8]. These factors all limit the direct usage of pyrolysis oil as a liquid transportation fuel. Several options have been proposed to convert bio-oils using conventional crude-oil technologies such as thermal- catalytic- cracking, hydrotreating, hydrocracking and aqueous phase processing [9-15]. Hydrogen based processes are typically more expensive than thermal cracking but they have the advantage that they produce products in higher selectivity, by minimizing light gas and coke formation. HDO involves the reaction of the bio-oil with hydrogen by four key classes of reaction (1) hydrogenation of C-O and C-C bonds, (2) dehydration of C-OH groups, (3) C-C bond cleavage by retro-aldol condensation and decarbonylation, and (4) hydrogenolysis of C-O-C bonds [1,16-18]. Typical process conditions for HDO include temperatures between 300 and 400 °C and hydrogen pressure between 507-4200 psi. However the high H₂ consumption and capital costs and low product selectivity render this method uneconomical [19,20]. Several previous papers have shown the challenge with obtaining high yields of products from HDO of bio-oil [12,19-23]. Direct hydrogenation (6 hr) of bio-oil in batch reactors over Raney Ni (200 °C, 40 bar H₂) yielded only 30% organic liquid (pH 3.3) indicating that the direct hydroprocessing of bio-oils is difficult and produces large yield of coke and tar, which lead to deactivation issues [24]. One of the catalyst deactivation mechanisms that occur during HDO of bio-oil is carbon deposition on the catalyst surface. This deactivation represents a major limit of this technology because the catalyst has to be frequently regenerated. One approach that has been reported is to try and develop HDO catalysts that have low acidity and hence a lower rate of coke formation [1,16]. Elliott and co-workers have reported that two hydrogenation steps are typically required for HDO of pyrolysis oil: 1) a low temperature step (100-140 °C) and 2) a high temperature step (200-300 °C) with final products containing 40% of the starting carbon [12,23]. The purpose of

the low temperature step is to hydrogenate aldehydes and ketones and make the pyrolysis oil more stable [21,25]. This low temperature stabilization step does not completely deoxygenate the bio-oil. However, it does make the pyrolysis oil more stable and decreases the rate of coke formation in the high temperature HDO step. The improved stabilization of the resulting bio liquid by the low temperature hydrogenation also allows the bio-oil to be easier to handle and store for further upgrading and applications in existing crude oil refinery settings [1]. The first step in the low temperature hydrogenation of the bio-oil is hydrogenation of guaiacols, hydroxyacetaldehyde, furfural, levoglucosan, furanone and phenol into more stable corresponding alcohols over Pt, Pd, Ru and Rh catalysts supported on carbon [21-23]. Vispute and Huber (2009) reported that 15% of the carbon is lost in solid and gas during hydrogenation of the bio-oil at 125 °C and that levoglucosan, sugars and aromatic rings are not fully converted to the corresponding alcohols at 125 °C [21]. Further, Li et al. converted an aqueous carbohydrate stream from maple wood into gasoline range products with carbon yield of 57% in a 2-step APP process over Ru/C catalyst (1st step) and Pt/ZrP catalyst (2nd step) [26]. These studies indicate that the challenge with WSBO hydrogenation is to minimize the H₂ consumption and carbon loss to the gas phase, while achieving high selectivity of the desired products. The use of continuous flow reactors is expected to improve the hydrogenation reaction due to higher concentration of hydrogen compared to batch reactors, since in the latter; the hydrogen availability is limited by the low H₂ solubility in water. Bio-oil aqueous phase hydrodeoxygenation (HDO) processes at moderate temperatures (≤ 250 °C) at which no catalyst coking or reactor plugging was observed were recently proposed to overcome the traditional hydro-treating limits and the single stage hydrogenation processes using moderate amounts of hydrogen and producing a range of products such as gasoline and feedstock for the chemical and

polymer industries [14]. The current bio-oil hydro-deoxygenation state of the art indicates that there is a wide range of products formed and that the involved catalytic chemistry needs to be understood in more detail [18,21,25]. These studies also illustrate the need to understand the homogeneous reactions that can also occur in the hydrogenation process. It would be highly desirable to be able to speciate the individual intermediates and identify the important reaction classes that occur in HDO of bio-oil.

The objective of this paper is to study the hydrogenation and HDO of a well characterised water soluble bio-oil in a packed bed with Ru/Carbon and Pt Carbon catalysts and identify the important reaction pathways. This paper provides important molecular level data about the reactions that occur during HDO of the aqueous phase of bio-oil. This molecular level knowledge can be used to design improved catalytic processes for the conversion of pyrolysis oils into fuels and chemicals.

2.0 Experimental and Materials

2.1 Bio-oil sample for APP

The bio-oil used was obtained from Mississippi State University. The bio-oil was produced by pyrolysis of dry pine wood in an auger reactor and was stored in a refrigerator to avoid aging. The bio-oil was separated into a water soluble bio-oil (WSBO) and water insoluble bio-oil (WIBO) fractions by the addition of water. About 112g of distilled water was mixed with 28g of bio-oil and then centrifuging at 10000 rpm for 20 minutes until phase separation. The centrifuge used was the Fisher Scientific Marathon 2100. The aqueous solution used in the experimental work had a WSBO concentration of 12.5wt%. Ash content of the bio-oil samples was 0.3wt%, found by heating about 1 gm of sample in a muffle furnace in the presence of air at 600-750 °C

for 6 hours. Nitrogen and sulphur were not detected by elemental analysis done at Galbraith Laboratories, Knoxville, Tennessee.

2.2 Catalytic APP hydrogenation set-up

A schematic of the packed bed reactor is shown in Figure 1. The reactors consist of a continuous flow reactor, a temperature controller system, a furnace and a hydrogen gas supply. The tubing connecting the sample flask to the reaction chamber was wrapped with silicone rubber insulated heating tape to maintain a temperature between 30 and 80 °C. The reactor was a ¼ inch in diameter tubing placed into a vertical furnace. Two different reactors were used in series during the experimental work, where the feed and hydrogen were added from the top of the reactors. A system of safety check valves and a back pressure regulator was installed for safety reasons. Digital mass flow controllers were used to control the gas flowrates.

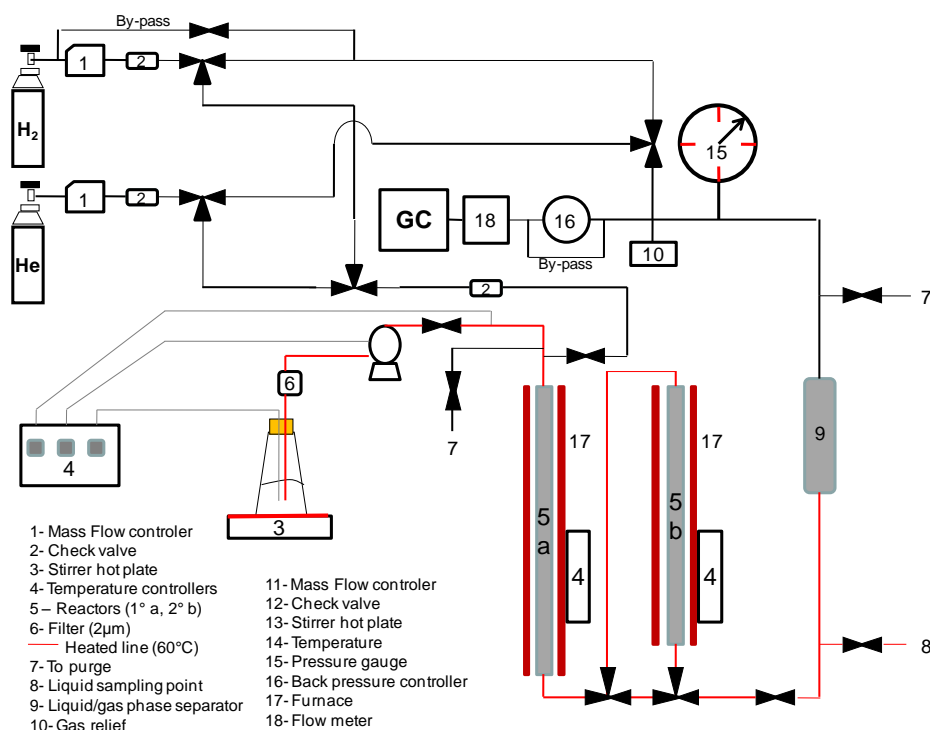


Figure 1 Scheme of down-flow reactor used for the bio-oil hydrogenation.

The WSBO was analyzed by GC-MS, High Performance Liquid Chromatography (HPLC) and Total Organic Carbon (TOC) analyzer to establish its composition. A library of 28 individual compounds was established to identify and semi-quantify the WSBO. The levoglucosan, glucose and sorbitol standards were analyzed by HPLC while all the other standard compounds (levoglucosan included) were detected and quantified by HP Gas Chromatograph (Model 7890A) with a Restek Rtx-VMS column using a constant column linear velocity of 1.24 mL/s. Ultra high purity helium was used as a carrier gas and the injection temperature was 280 °C. The program involved a hold at 35 °C for 5 minutes, followed by a rise to 240 °C at 10 °C/min and a hold at 240 °C for 15 minutes. The HPLC was packed with a Bio-Rad's Aminex HPX-87H column with 0.0005M sulphuric acid as mobile phase (flow rate of 1ml/min) at 30 °C. The HP Gas Chromatograph (Model 7890A) was used to analyze the reactor effluent gas, the liquid feed and liquid products. The effluent gas was analyzed using a flame ionization detector (FID) maintained at 300 °C. A Restek RT-Q-BOND column was used with a helium carrier gas flowing at 4.24 ml/min. The column oven temperature programme involved a hold at 30 °C for 5 min, a ramp to 150 °C at 5 °C/min and a hold at 150 °C for 15 min. The liquid product was sampled every 4 or 8 hours to be analyzed by GC-FID and HPLC. At least 3 liquid samples were collected at a particular set of operating conditions to ensure the steady state. The quantification of sugars, sugar/alcohols and levoglucosan was carried out using a Shimadzu HPLC system. A flame ionization detector (FID) was used on the GC to quantify all the other liquid products. A GC-TCD HP 5890 series II was used to analyse CO₂ and hydrogen with an Alltech HAYESEP DB 100/120 packed column with 1ml/min of helium as carrier gas. The oven temperature was maintained at 75 °C and the injection ports at 160 °C and 120 °C for CO₂ analysis, respectively. Standards of methane, ethane, propane, butane, pentane (FID) and CO₂ (TCD) were used to

identify and quantify the gas produced. The carbon content was analyzed by a Shimadzu 5000A Total Organic Carbon (TOC) that was able to quantify carbon contents below 1000ppm. The aqueous phase hydrogenation experiments were carried out using a stainless tubular downward flow reactor heated by a Lindberg Blue M furnace. The temperature was maintained with an in-built temperature controller on the furnace. The catalysts used were (i) 5 wt% ruthenium/ activated carbon (Strem Chemicals, Product No. 44-4059) and (ii) 5 wt% platinum/ activated carbon (Strem Chemicals, Product No. 78-1509). Both catalysts were in wet form, about 50wt% water, and were dried at 110 °C for 7 hr using 3 L/min of nitrogen before every reaction cycle. The hydrogen uptake of the Ru/Carbon catalyst was measured as 33.2 $\mu\text{mol H atoms/g dry catalyst}$ [21].

Between 0.8 to 1.6 g of catalyst was packed into the tubular reactor and secured using glass wool. The packing was important to create a homogeneous flow of feed and hydrogen through the catalyst and also to eliminate void space in the reactor to suppress homogeneous reactions. A 50% void space was used in the experiments which studied temperature effect in the single catalyst zone. The catalyst was reduced in situ under a constant hydrogen flow of 150 ml/min while heated to 260 °C at 0.5 °C/min. The catalyst was then held at 260 °C for 2 hours and then cooled to ambient temperature. After this, the reactor pressure was set to 750 or 1445 psi by a back pressure regulator. The liquid feed was co-fed from the top of the reactors together with the hydrogen at different feeding rates of 0.02, 0.04, 0.08, or 0.16 ml/min using an Eldex Laboratories 1SM HPLC pump. The above flow rate corresponded to a Weight Hourly Space Velocity (WHSV) of 0.75 h^{-1} , 1.5 h^{-1} , 3 h^{-1} and 6 h^{-1} , respectively, where WHSV represents the mass flow rate of the liquid feed divided by the amount of catalyst.

A 0.2 μm particulate filter (Swagelok, Product No. SS-2F-T7-2) was placed between the feed

container and the pump to remove small char particles from the bio-oil. A gas/liquid phase separator was used after the reactors and the liquid samples were sampled at this point. The gas products went through the back pressure regulator and were analyzed by GC FID and TCD. The bio-oil hydrogenation was tested at the temperatures 75, 100, 125, 150, 175, 200, 220, 250 and 275 °C. The stability of catalysts was investigated for 100 hr.

3.0 Results and Discussion

3.1 Bio-oil catalytic hydrogenation in a single stage

3.1.1 Bio-oil composition

The water soluble fraction of the bio-oil (WSBO) used in this work had a range of different oxygenated compounds as shown in Figure 2. The major compounds in the water soluble bio-oil include: levoglucosan > hydroxyacetaldehyde > catechol > acetic acid > hydroxyacetone > and glucose. These compounds represented 65 carbon% of the total composition. Small amounts of 5-HMF, 3-methyl-1,2-cyclopentanedione, 2(5H)-furanone, guaiacol and phenol were also detected. The bio-oil is highly oxygenated and has a range of functionalities like aldehydes, ketones, carboxylic acids, sugars and aromatics. One third of the carbon in the WSBO could not be detected by our GC and HPLC techniques. This fraction is probably lignin and carbohydrate oligomers [27].

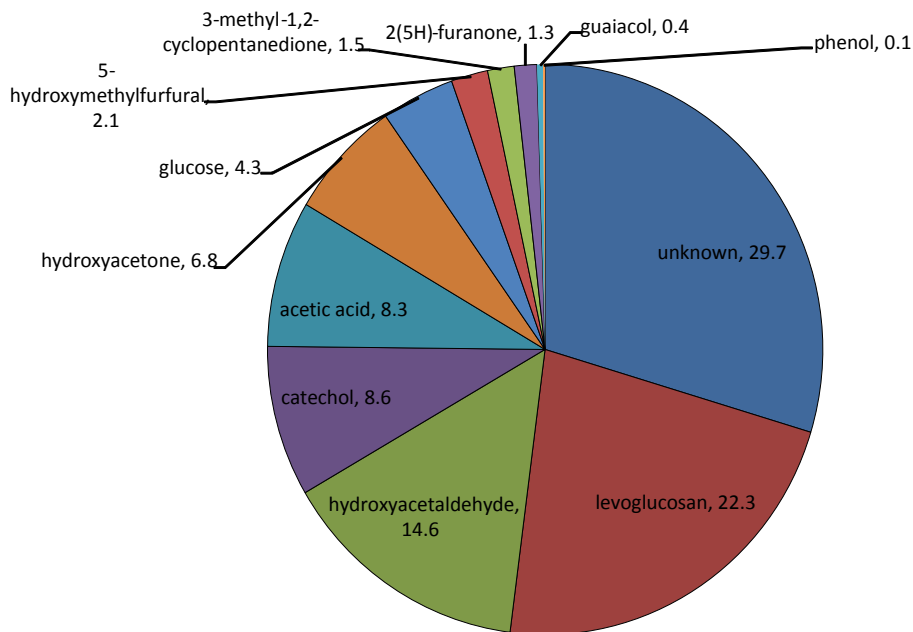


Figure 2 Concentration of organic compounds (Carbon %) in the WSBO (excluding water). This bio-oil was used as feed material for the APHDO experiments.

3.1.2 Homogeneous Reactions

The WSBO was tested in the continuous flow reactor at similar flow rates used in our hydrogenation conditions without a catalyst to study the effects of homogeneous reactions.

Figure 3 shows the concentration of components in the WSBO before after reactions at 125°C and 150°C for 36 hr in the presence of hydrogen without any catalyst. The hydroxyacetaldehyde, levoglucosan, sugar and catechol concentrations decreased with increasing reaction temperature. The acetic acid, hydroxyacetone, furfural, 5-hydroxymethylfurfural (HMF), phenol (not shown), and guaiacol (not shown) concentrations either increased or did not change with increasing reactions temperature. At 150°C, 90%, 40% and 20% of the levoglucosan, hydroxyacetaldehyde and sugars respectively were converted by homogeneous degradation reactions. The concentrations of phenol, catechol and acetic acid were the same in the product and the feed at both 125 and 150°C. At 150°C, the concentration of hydroxyacetone, furfural and 5-HMF

increased by 0%, 25% and 30%, respectively. These products are all produced from the dehydration of levoglucosan [28]. Coking reactions took place at 150 °C, with the conversion of sugars into carbon deposits by polymerization and condensation reactions. Oligomers with mass ranging from 100 to 10,000 Da are present in the WSBO used in this work [14]. Glucose can also react with lignin oligomers that can be present in WSBO [29,30]. At 150°C, the reactor plugged with a black tar-like material being formed after 24 hrs time on stream. This suggests that low temperature catalytic hydrogenation of bio-oil should be carried out below 150 °C in the absence of void space (i.e. the reactor should be completely filled with catalyst) in the reactor to avoid carbon deposition reactions. No measurable hydrogenation of the bio-oil occurred without a catalyst, even with high hydrogen concentration.

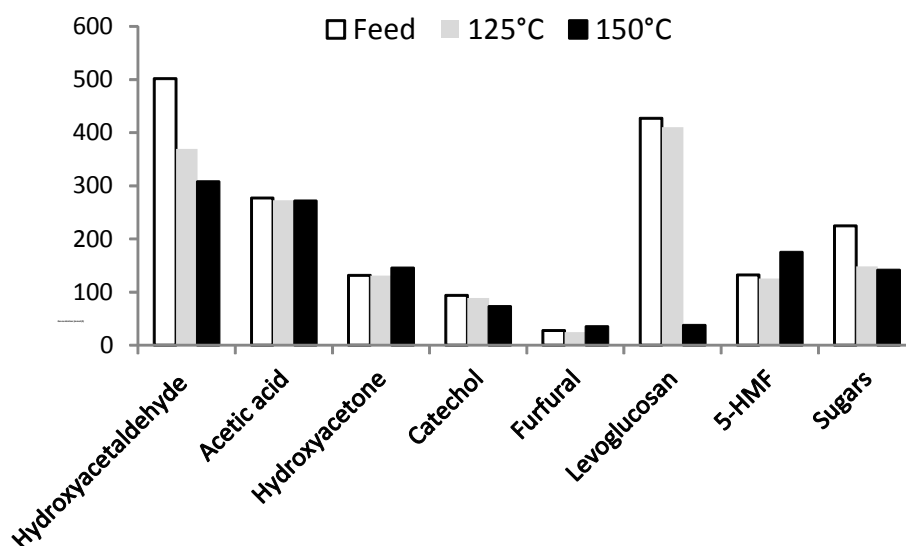


Figure 3 Homogeneous reactions of water soluble bio-oil phase. P: 750 psi, WHSV: 1.5 h⁻¹ and a hydrogen flow rate of 150 ml/min.

3.1.3 Temperature effect for Low temperature Hydrogenation

The WSBO was hydrogenated at temperatures from 75 to 175°C in a continuous flow reactor with a Ru/Carbon catalyst as shown in Table 1. This set of experiments was carried out with 50% void space in the reactor where the void space was before the catalyst bed. In batch phase hydrogenation of WSBO, a large amount of carbon is lost to the gas phase forming primarily methane and CO₂ [21]. At 75 and 100 °C, only 4 and 15% of the identified reactants were converted into products. The reactants which converted at these temperatures were 2-furanone, furfural, 5-HMF, hydroxyacetaldehyde and methyl-cyclopentanedione. At 125 °C, 56% of the reactants were converted. The reactants that were converted at this temperature include hydroxyacetone, catechol, phenol, levoglucosan and sugars. The conversion of all the reactants, except acetic acid and phenol, was almost complete (90%) when the temperature was raised to 150°C. At 175°C, the reactor plugged, after 8 hrs time on stream, due to homogeneous coking reactions. About 19% and 22.5% of the starting carbon was deposited as coke at 150 and 175°C, respectively. These carbon depositions occur in the free section of the reactor, where the catalyst was not present.

The product distribution for the hydrogenation of the WSBO is shown in Table 1. The most abundant products in the liquid phase are ethylene glycol (EG) > propylene glycol (PG) > butyrolactone > sorbitol > 1,4 and 1,2 butanediol > 1,2-cyclohexanediol > tetrahydrofurfuryl alcohol (THF) > glycerol and > methanol. Other identified products include ethanol, propanol, butanol, pentanal, cyclopentanol, cyclohexanol, valerolactone, methane, ethane, propane and finally butane. According to Table 1 there is a clear effect of temperature on the hydrogenation reactions. The EG concentration is highest at 100 °C and 125 °C and then decreases at higher temperature probably due to cleavage of C-O and C-C bonds with formation of light gases.

Similarly, the PG concentration is highest at 150 °C and then decreases. The amount of carbon converted into the gas phase products (CH_4 and C_2H_6) increased from 0.5% (75°C) to 14% (175°C) as the temperature increased. We choose to do future experiments in this paper at 125 °C because of the high product selectivity observed at this temperature.

Table 1 Product selectivity for hydrogenation of WSBO over Ru/C as a function of temperature. Catalyst: 5wt% Ru/C, WHSV: 3 h⁻¹, P: 750 psi, H₂ flow rate: 150 ml min⁻¹, Feed: ~13wt% WS-PWBO solution in water.

Reactants	Concentration, mmol-C/L					
	Feed	75°C	100°C	125°C	150°C	175°C
Hydroxyacetaldehyde	376.2	386.2	233.2	24.9	0.0	0.0
Acetic acid	191.9	205.2	203.9	161.2	166.6	172.1
Hydroxyacetone	160.9	196.4	203.8	67.4	5.8	0.0
2(5H)-Furanone	34.1	3.7	4.1	11.6	8.9	1.1
Phenol	2.2	2.2	2.2	1.4	1.4	1.5
3-Methyl-1,2-cyclopentanedione	43.4	37.2	23.3	0.0	0.0	0.0
Guaiacol	9.4	8.8	9.1	8.3	0.0	4.0
Catechol	247.1	237.4	218.2	108.1	33.1	13.5
Furfural	17.8	5.2	4.9	0.0	0.0	0.0
5-HMF	57.4	23.6	15.6	6.4	0.0	0.0
Levoglucosan	602.4	582.5	553.2	280.8	0.0	0.0
Sugars	171.9	153.8	148.7	163.3	4.8	0.9
Products						
Methanol	15.1	34.0	40.6	23.1	22.1	16.0
Ethanol	0.0	3.1	3.6	8.9	10.1	10.8
1-Propanol	0.0	3.9	2.2	4.0	6.8	8.7
Butanol	0.0	0.0	0.0	2.6	3.2	4.3
Pentanol	0.0	0.0	0.0	0.0	0.0	2.7
Ethylene glycol	0.0	139.8	287.0	275.5	185.6	128.9
Cyclopentanol	0.0	0.0	0.0	2.0	5.6	7.7
Propylene glycol	0.0	3.5	4.8	76.4	121.8	110.5
Cyclohexanol	0.0	0.0	0.0	3.5	37.3	38.1
1,2-Butanediol	0.0	0.0	0.0	23.1	49.2	30.0
Tetrahydrofurfuryl alcohol	0.0	10.0	11.2	10.8	18.0	23.6
1,4-Butanediol	0.0	2.8	11.5	33.6	27.8	17.7
γ-Butyrolactone	0.0	54.2	57.3	55.0	72.7	60.5
γ-Valerolactone	0.0	0.0	0.0	4.1	7.0	8.7
Glycerol	0.0	13.4	16.7	10.0	11.6	5.4
1,2-Cyclohexanediol	0.0	0.0	0.0	2.6	32.0	33.0
R-γ-Hydroxymethyl-γ-butyrolactone	0.0	22.1	22.7	29.2	27.7	17.0
Methane	0.0	259.4	288.1	353.5	537.8	620.9
Ethane	0.0	54.7	56.6	61.9	80.5	129.4
Sorbitol	0.0	48.8	37.7	36.0	67.2	12.1
Carbon identified (GC-MS, HPLC)	1929.7	2491.8	2460.1	1849.2	1544.5	1478.9
Total Carbon in liquid (TOC)	2633.3	2519.6	2539.0	2451.5	1971.2	1680.9
%Carbon to liquid phase		95.5	96.4	93.1	74.9	63.8
%Carbon lost to gas phase		0.5	0.5	1.1	6.3	13.8
%Carbon lost to solid phase		3.0	3.1	5.8	18.8	22.4

3.1.4 Catalyst stability

The catalyst stability was evaluated by doing the hydrogenation experiments with the WSBO with Ru/C catalyst at 125 °C for a 3 day period. Figure 4 shows the concentration of the main

hydrogenation products as a function of time on stream. The major products were ethylene glycol, propylene glycol, methanol and ethanol. No signs of deactivation (loss of activity, pressure build up, etc) were observed in the more than 80 hrs of testing of this catalyst.

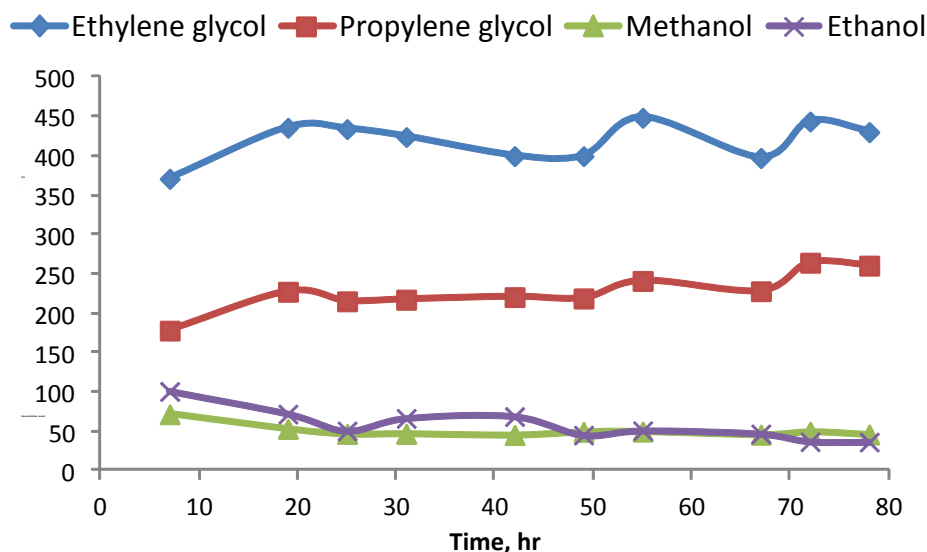


Figure 4 Outlet concentrations as a function of time on stream for APH of WSBO at 125 °C, 750 psi of H₂ and WSBO feed flow rate of 0.04 ml/min.

3.1.5 Effect of feed residence time

The effect of the residence time was investigated using different feed space velocities at 125°C using 4 different weight hourly space velocities (WHSV) as reported in Table 2. The reactant conversion increased with decreasing WHSV from 56.5% at a WHSV of 6.0 h⁻¹ to 85% at velocity WHSV of 0.75 h⁻¹. HMF, furfural, and guaiacol were completely converted at a WHSV of 6 h⁻¹. Hydroxyacetaldehyde and hydroxyacetone were almost completely converted at this same WHSV. Among the aromatics' conversion, catechol was found to be the least reactive. However, the concentration of catechol was much higher than the others aromatic compounds. The conversion of acetic acid, sugars and levoglucosan was low at a WHSV of 6 h⁻¹. The acetic acid conversion did not increase even with decreasing space velocity. The conversion of

levoglucosan and other sugars increased with decreasing feed flow rates up to 90% conversion at a WHSV of 0.75 h^{-1} . A total identified reactants conversion of 70.2% was obtained at the intermediate WHSV of 3.0 h^{-1} .

Table 2 Effect of liquid space velocity on reactants and product selectivity for APH of bio-oil at 125 °C, 750 psi and a hydrogen flow rate of 150 ml/min

Reactants	Concentration, mmol-C/L				
	Feed	0.75 h ⁻¹	1.5 h ⁻¹	3.0 h ⁻¹	6.0 h ⁻¹
Hydroxyacetaldehyde	427.6	0.0	0.0	0.0	13.8
Acetic acid	244.1	213.4	220.2	203.2	211.7
Hydroxyacetone	199.3	0.0	0.0	0.0	14.3
2(5H)-Furanone	37.6	27.9	27.2	21.6	16.0
Phenol	2.5	0.0	0.0	0.0	0.2
3-Methyl-1,2-cyclopentanedione	45.7	0.0	0.0	0.0	1.8
Guaiacol	10.3	0.0	0.0	0.0	0.0
Catechol	208.1	0.0	0.0	0.0	65.3
Furfural	20.9	0.0	0.0	0.0	0.0
5-Hydroxymethylfurfural	63.9	0.0	0.0	0.0	0.0
Levogluconan	652.5	57.7	152.2	341.8	443.1
Sugars	124.4	13.4	56.7	43.1	123.6
Products					
Methanol	24.4	70.2	49.0	49.1	49.9
Ethanol	0.0	47.8	18.2	19.7	16.8
1-Propanol	7.9	37.1	8.3	9.7	8.0
Butanol	0.0	13.1	4.6	4.4	3.9
Pentanol	0.0	4.1	0.0	0.0	0.0
Ethylene glycol	0.0	450.6	413.2	498.0	495.7
Cyclopentanol	0.0	18.0	15.5	9.5	12.2
Propylene glycol	0.0	195.3	186.9	183.3	190.4
Cyclohexanol	0.0	120.0	122.2	124.6	74.2
1,2-Butanediol	0.0	56.4	74.0	32.1	23.5
Tetrahydrofurfuryl alcohol	0.0	29.8	18.8	1.0	2.7
1,4-Butanediol	0.0	32.8	48.8	54.2	52.5
Y-butyrolactone	0.0	122.9	148.7	154.5	125.2
Y-valerolactone	0.0	9.5	8.6	9.6	3.0
Glycerol	0.0	45.6	19.4	30.5	28.0
1,2-Cyclohexanediol	0.0	102.8	106.9	63.7	104.8
Y-Hydroxymethyl-Y-butyrolactone	0.0	19.7	66.0	70.1	69.3
Sorbitol	43.8	497.4	602.4	386.9	186.2
Carbon identified (GC-MS, HPLC)	2154.7	3556.6	2884.6	2731.7	2486.4
Total carbon in liquid (TOC)	3879.3	3356.2	3634.7	3590.3	3669.3
%Carbon to liquid phase		86.5	93.7	92.5	94.6
%Carbon to gas phase		13.5	6.3	7.5	5.4

The amount of feed converted into gas phase (C1 to C4) products increases with decreasing WHSV. The experiment at a WHSV of 0.75 h⁻¹ was able to retain 87% of the carbon in the liquid phase with 13.5% of the carbon converted to gas phase products, with methane being the major

gas phase product. At the space velocities of 1.5 to 6 h⁻¹, the carbon loss to gas phase products is essentially the same at around 6%.

The reaction products can be also divided in 4 different categories in terms of chemical functionalities: mono-alcohols, alkanes, diols, polyols and cyclic ethers. Diols are the largest group of compounds, besides methane, at low WHSV. The diols observed in decreasing concentration are ethylene glycol >propylene glycol >butanediol. The mono-alcohol concentration decreases with increasing MW of the monoalcohol with no hexanols being observed as products. The alkane distribution is a function of WHSV with methane being the alkane produced in highest concentration. The product distribution is influenced by the WHSV. The alkanes decrease with increasing WHSV whereas most of the diols slightly decrease with increase WHSV. The concentration of mono-alcohols increases with decreasing WHSV. This suggests that at low WHSV the diols are converted into alkanes and alcohols. Ethylene glycol and propylene glycol are most likely produced from hydrogenation of hydroxyl acetaldehyde and hydroxyl acetone, respectively. However, the concentration of ethylene glycol is higher than the concentration of hydroxyacetaldehyde in the feed implying that another reactant also produced ethylene glycol [31,32]. Cyclohexanol and 1,2-hexanediol are probably produced from guaiacol and catechol hydrogenation, respectively as has previously been observed by Elliot and co-workers [12]. The gamma-butyrolactone (γ -GBL) concentration is higher than stoichiometrically possible from furfural and 2-(5H)-furanone. This extra source of γ -GBL is unknown. The sorbitol concentration reaches a maximum at WHSV of 1.5 h⁻¹. Sorbitol undergoes secondary reactions at the space velocity of 0.75 h⁻¹ with methane being the primary product.

3.2 Catalytic hydrogenation of bio-oil in two stages

3.2.1 Two stage process

A set of experiments using two different reactors connected in series was done as shown in Tables 3 and 4. In all these experiments Ru/C was used in the 1 stage and either a Ru/C or Pt/C catalyst was used in the second reactor stage. The two stage processes were able to convert 26-28% more of the feed than the single stage process. The conversion of acetic acid, the most difficult compound to be hydrogenated, was successfully increased from 17% to 59% and 75% (best cases) during the two steps process using platinum and ruthenium. However, the acetic acid conversion was similar to the conversion obtained in the single step process at 200 and 220 °C.

Tables 3 and 4 compare the concentration of the feed and product compounds and the overall mass balance of the experiments. A larger distribution of liquid products is produced with platinum than ruthenium. The platinum-carbon catalyst was able to retain 70% and 80% of the carbon in the liquid phase at 220 °C and 250 °C, respectively. The liquid yield at 220 °C was increased from 80 % to 90% by increasing reaction pressure from 750 psi to 1445 psi. In contrast the liquid yield with Ru/C was 70% at 220 °C and decreased to 38% at 250 °C. High hydrogen pressure suppressed the gaseous product formation with the Pt catalyst. The gas yield at 220 °C was 5 fold lower at 1445 psi compared to 750 psi. Levoglucosan and the sugars are readily converted under the process conditions into sorbitol, EG, PG, butanediol, ethanol, methanol and other compounds. Levoglucosan disappearance is not accompanied by a corresponding increase in sorbitol concentration. This implies that the sorbitol undergoes hydrogenolysis producing EG, PG, butanediols and glycerol at similar rates that the levoglucosan is converted into sorbitol. The yield of sorbitol, EG and methanol show higher selectivity at lower temperature of 200 °C, whereas PG and butanediol are much more selectively produced at 220 °C with Pt in the 2nd

reactor. Moreover, ethanol has a higher concentration at 250 °C probably due to higher conversion of acetic acid at that temperature. Furfural, HMF and 2-furanone are completely converted at all the investigated temperatures. Butyrolactone and hydroxy-methyl-butyrolactone concentrations peak at 220 °C and then start to disappear due to their conversion into furan-tetrahydro and furan-tetrahydro-2-methyl. This hydrogenation reaction is characterised by the hydrogenation –dehydration of C-O bonds favoured at these high temperatures and in acid environment probably by acid catalysed reactions.

Table 3 Product composition for the HDO of WSBO in a two bed reactor system with Ru/C in both beds. (1.7 g catalyst 1st reactor + 1.7 g in 2nd reactor, H₂ flow rate 150 ml/min, H₂ pressure 750 psi, WHSV of 3 hr⁻¹ and 6 h⁻¹).

Reactants	Feed	Concentration, mmolC/L			
		750psi, 3h ⁻¹	750psi, 3h ⁻¹	750psi, 3h ⁻¹	750psi, 6h ⁻¹
		125-200 °C	125-250 °C	125-220 °C	125-250 °C
Hydroxyacetaldehyde	469.34	0.00	0.00	0.00	0.00
Acetic acid	182.83	169.36	45.93	170.59	178.56
Hydroxyacetone	158.84	0.00	0.00	0.00	0.00
2(5H)-Furanone	34.54	0.00	0.00	0.00	0.00
Phenol	2.18	0.00	0.00	0.00	0.00
3-Methyl-1,2-cyclopentanedione	39.66	0.00	0.00	0.00	0.00
Guaiaicol	9.55	0.00	0.00	0.00	0.00
Catechol	192.59	0.00	0.00	0.00	0.00
1-Hydroxy-2-butanone	17.90	0.00	0.00	0.00	0.00
Furfural	21.19	0.00	0.00	0.00	0.00
2-Cyclopenten-1-one	20.85	0.00	0.00	0.00	0.00
5-Hydroxymethylfurfural	55.04	0.00	0.00	0.00	0.00
Pentanal	21.81256	0.00	0.00	0.00	0.00
4-Methylcatechol	123.32	0.00	0.00	0.00	0.00
Levogluconan	578.11	3.93	0.00	0.00	0.00
Sugars	187.4	7.49	0.00	3.92	9.32
Products					
Methanol	15.26	86.31	49.78	44.83	42.34
Ethanol	0.00	41.62	66.91	27.71	21.02
1-Propanol	0.00	39.55	52.09	28.12	29.56
Furan, tetrahydro	0.00	14.90	38.83	11.51	9.45
2-Butanol	0.00	5.84	27.50	8.27	12.45
Furan, tetrahydro-2-methyl	0.00	17.01	38.23	22.11	27.71
Furan, tetrahydro-2,5-dimethyl	0.00	15.90	40.17	20.19	22.59
1-Butanol	0.00	12.33	21.54	14.08	14.78
2-Pentanol	0.00	8.12	31.64	7.34	5.63
1-Pentanol	0.00	3.77	9.64	9.66	8.88
Ethylene glycol	0.00	200.81	5.13	174.88	260.14
Cyclopentanol	0.00	20.09	52.94	19.50	18.16
2-Hexanol	0.00	2.74	14.46	4.29	1.39
Propylene glycol	0.00	106.65	16.72	177.19	193.71
2,3-Butanediol	0.00	32.84	44.94	32.87	25.35
Cyclohexanol	0.00	48.79	76.62	44.84	44.02
1,2-Butanediol	0.00	83.92	0.00	109.75	92.47
Tetrahydrofurfuryl alcohol	0.00	12.30	21.82	34.98	32.50
1,4-Butanediol	0.00	15.62	29.74	18.94	16.09
Y-Butyrolactone	0.00	38.43	9.31	82.76	84.37
Y-Valerolactone	0.00	7.15	5.65	14.19	13.78
Glycerol	0.00	31.91	0.00	19.20	24.08
1,2-Cyclohexanediol	0.00	66.19	34.80	69.80	66.76
Y-Hydroxymethyl-Y-butyrolactone	0.00	16.23	0.00	46.40	69.64
Sorbitol	0.00	381.17	0.00	167.52	259.11
CH ₄	0.00	64.13	1039.02	296.55	29.28
C ₂ H ₆	0.00	21.15	751.41	172.10	12.39
C ₃ H ₈	0.0	10.92	482.76	63.83	5.96
C ₄ H ₁₀	0.0	6.16	214.12	21.43	6.92
C ₅ H ₁₂	0.0	7.02	84.76	19.08	10.52
C ₆ H ₁₄	0.0	22.05	85.05	40.75	24.95
Cyclopentanol, 3-methyl	0.0	26.19	37.69	33.86	20.94
1,2,3-Butanetriol	0.0	16.81	46.95	52.78	45.79
2H-Pyran-2-methanol, tetrahydro	0.0	15.23	42.08	21.25	17.55
1,4-Pentanediol	0.0	17.11	26.44	14.81	15.19
Cyclohexanol, 3-methyl	0.0	11.31	30.70	39.09	39.86
Cyclohexanol, 4-methyl	0.0	13.27	17.59	7.54	9.90
1,2-Hexanediol	0.0	10.15	25.61	50.69	38.91
1,2,6-Hexanetriol	0.0	23.05	5.87	14.22	5.96
Carbon identified (GC-MS, HPLC)	2130.4	1755.5	3624.4	2233.4	1868.0
Total Carbon in liquid (TOC)	3695.8	2772.8	1416.7	2637.5	2991.7
% carbon to liquid phase		75.0	38.3	71.4	80.9
% carbon to gas phase		25.0	61.7	28.6	19.1

The hydrogenation reactions further produce linear alcohols such as butanol that is further converted into light alkanes, such as butane at higher temperatures. These results clearly show that temperature is a critical parameter to tailor the selectivity of the desired products. The abundance of mono-alcohols, such as ethanol, propanol, cyclopentanol and cyclohexanol and dehydrated compounds such as furan substitutes, was found to be high at high WHSV. On the contrary, the concentration of compounds with higher boiling point such as EG, PG, sorbitol and cyclohexanediol was higher at low WHSV. This clearly indicates that the selectivity of the hydrogenation products can be controlled by increasing or decreasing the residence time. It has been shown that the C-C bonds cleavage rate on platinum is 7 times less than on ruthenium for ethylene glycol aqueous phase reforming [33]. Platinum showed a high C-O hydrogenation and low C-C bond cleavage activity for HDO of sorbitol [17]. Also, Pt can catalyze glycerol hydrogenolysis to propylene glycol more selectively than Ru. Ru mainly produces ethylene glycol and methane for glycerol conversion due to its high activity for C-C bond cleavage [34].

At 220°C, both levoglucosan and sugars are readily converted under the process conditions into mainly sorbitol, which undergoes further hydrogenolysis reactions producing EG, PG, butanediols, ethanol, methanol and other mono-alcohols. This sorbitol was converted by increasing the 2nd stage hydrogenation temperature to 250°C, leading to about 25% of gaseous products and converting 41% of the carbon into gasoline additives (24%) and diols (17%). The carbon loss in the gas phase was reduced to only 12% by increasing the operating pressure to 1445 psi.

Table 4, Product composition for the HDO of WSBO in a two bed reactor system with Ru/C (1.7 g catalyst) in the 1st reactor and Pt-C (1.7 g catalyst) in 2nd reactor, H₂ flow rate 150 ml/min, H₂ pressure 750-1450 psi, WHSV of 3 hr

Reactants	Feed	Concentration, mmolC/L				
		750psi, 3h ⁻¹	750psi, 3h ⁻¹	1450psi, 3h ⁻¹	1450psi, 3h ⁻¹	1450psi, 3h ⁻¹
		125-220 °C	125-250 °C	125-220 °C	125-250 °C	125-275 °C
Hydroxyacetaldehyde	454.5	0.0	0.0	0.0	0.0	0.0
Acetic acid	144.8	120.5	59.4	133.3	104.9	56.8
Hydroxyacetone	144.8	0.0	0.0	0.0	0.0	0.0
2(5H)-Furanone	37.2	0.0	0.0	0.0	0.0	0.0
Phenol	2.3	0.0	0.0	0.0	0.0	0.0
3-Methyl-1,2-cyclopentanedione	31.9	0.0	0.0	0.0	0.0	0.0
Guaiacol	8.8	0.0	0.0	0.0	0.0	0.0
Catechol	36.2	0.0	0.0	0.0	0.0	0.0
1-Hydroxy-2-butanone	20.2	0.0	0.0	0.0	0.0	0.0
Furfural	18.0	0.0	0.0	0.0	0.0	0.0
2-Cyclopenten-1-one	21.9	0.0	0.0	0.0	0.0	0.0
5-Hydroxymethylfurfural	50.8	0.0	0.0	0.0	0.0	0.0
Pentanal	26.1	0.0	0.0	0.0	0.0	0.0
4-Methylcatechol	47.5	0.0	0.0	0.0	0.0	0.0
Levogluconan	489.2	4.4	0.0	0.0	0.0	0.0
Sugars	159.4	6.6	4.4	10.4	6.5	4.08
Products						
Methanol	17.2	53.3	66.8	48.4	56.8	80.1
Ethanol	0.0	45.4	133.7	31.6	47.9	115.5
1-Propanol	0.0	34.1	80.2	18.7	42.5	59.8
Furan, tetrahydro	0.0	9.0	21.4	6.0	6.1	9.8
2-Butanol	0.0	8.6	13.1	7.6	15.0	17.9
Furan, tetrahydro-2-methyl	0.0	17.0	23.3	15.5	21.5	22.0
Furan, tetrahydro-2,5-dimethyl	0.0	18.9	25.6	14.4	19.7	17.0
1-Butanol	0.0	14.5	31.7	8.2	11.7	19.8
2-Pentanol	0.0	6.6	13.5	3.1	4.4	5.9
1-Pentanol	0.0	4.7	26.9	5.2	8.4	15.7
Ethylene glycol	0.0	355.5	192.2	414.8	465.1	189.6
Cyclopentanol	0.0	22.9	48.7	18.9	23.0	27.0
2-Hexanol	0.0	5.3	24.3	4.0	7.9	10.1
Propylene glycol	0.0	198.6	221.1	212.1	317.3	218.2
2,3-Butanediol	0.0	35.9	44.8	27.4	34.9	31.0
Cyclohexanol	0.0	75.8	77.0	51.9	51.3	41.1
1,2-Butanediol	0.0	75.3	100.6	83.0	137.4	111.1
Tetrahydrofurfuryl alcohol	0.0	40.4	94.8	18.8	72.7	132.9
1,4-Butanediol	0.0	41.5	34.4	58.3	68.6	33.9
γ-Butyrolactone	0.0	80.8	92.8	119.6	110.6	111.4
γ-Valerolactone	0.0	11.9	15.8	11.8	12.5	13.8
Glycerol	0.0	42.7	0.0	41.9	48.8	1.8
1,2-Cyclohexanediol	0.0	91.0	72.3	114.4	107.7	62.7
γ-Hydroxymethyl-γ-butyrolactone	0.0	43.6	0.0	74.2	47.0	25.2
Sorbitol	0.0	510.6	0.0	591.8	21.8	0.0
CH ₄	0.0	277.0	584.2	59.8	103.2	111.4
C ₂ H ₆	0.0	36.6	58.0	6.5	10.0	28.2
C ₃ H ₈	0.0	27.3	37.7	5.5	14.7	19.5
C ₄ H ₁₀	0.0	10.5	16.6	2.1	5.4	9.9
C ₅ H ₁₂	0.0	15.9	19.8	4.5	14.5	18.0
C ₆ H ₁₄	0.0	129.0	131.0	30.8	115.4	121.2
Cyclopentanol, 3-methyl	0.0	23.7	43.8	20.2	33.9	36.5
1,2,3-Butanetriol	0.0	10.2	15.9	23.7	29.2	27.1
2H-Pyran-2-methanol, tetrahydro	0.0	23.4	38.3	20.7	32.9	32.2
1,4-Pentanediol	0.0	19.4	30.6	15.7	23.3	19.2
Cyclohexanol, 3-methyl	0.0	18.8	34.7	22.1	34.3	32.4
Cyclohexanol, 4-methyl	0.0	14.8	24.3	14.9	20.5	15.8
1,2-Hexanediol	0.0	7.8	16.1	21.4	27.7	19.3
1,2,6-Hexanetriol	0.0	12.4	0.0	15.5	14.2	0
Carbon identified (GC-MS, HPLC)	1711.0	2602.3	2570.3	2408.7	2351.3	1924.6
Total Carbon in liquid (TOC)	4005.9	3223.9	2881.1	3616.1	3405.3	2570.3
% carbon to liquid phase		80.5	71.9	90.3	85.0	64.2
% carbon to gas phase		19.5	28.1	9.7	15.0	35.8

The concentration of diols such as ethylene glycol, propylene glycol and butanediol increased considerably when the H₂ pressure increased to 1445 psi, while mono-alcohols, such as ethanol and methanol, decrease in abundance due to the suppression of secondary hydrogenation reactions of diols. The desired products yield increased to 46% under these conditions with large fraction of diols being formed (29%) and lower yield of gasoline cuts (17%), compared to the experiment at 750 psi.

These findings indicate that it is possible to control the hydrogenation reactions and thus selectively producing target compounds such diols, gasoline additives or alkanes (at 275°C), by changing the pressure, WHSV and temperature in the process. However, the conversion of acetic acid was not been complete even under these higher temperatures.

3.2.3 Product selectivity and catalysts comparison

The overall goal of the hydrogenation process is to produce fuels and chemicals from the aqueous fraction of bio-oil. Bio-oil is a complex mixture of hundreds of compounds and the resulting upgraded liquid still is a complex mixture. Therefore, a distillation is probably the best option to separate the products into a few different boiling fractions similar to a crude-oil refinery. Table 5 and Figure 5 illustrate all the products grouped by chemical functionality of after the 1-stage and 2-stage process in presence of only Ru/C (Table 5) and Ru/C and Pt/C catalysts (Figure 5). The compounds present in the hydrogenated bio-oil can be divided into nine groups based on their chemical functionality: C1-C4 alkanes and other gas products, gasoline cut1 (mono-alcohols with BP 60-100 °C), gasoline-cut 2 (mono-alcohols with BP 115-160 °C), C2-C6 diols, lactones, acetic acid, sorbitol, other chemicals and unidentified compounds. Less than 30% of the carbon in the feed is converted to gasoline additives and diols in the single stage process with ruthenium at 125°C and WHSV of 3 hr⁻¹.

At higher temperature (220-250°C) levoglucosan and sorbitol are successfully converted with Ru, however the yield of their primary hydrogenation products (e.g. PG, EG) did not increase. This indicates that the carbohydrate primarily were converted into methane with Ru/Carbon. The gas phase carbon reached a max yield of 62% at 250°C and 750 psi with Ru/C. Operating at higher space velocities can decrease the gas phase carbon products to about 20% with Ru/C (6 hr⁻¹, 750psi, 250°C), but this reduces the carbon yield of desired gasoline products and diols at 16%, less than the 1-step process. Considering the low yield of desired products, Ru/C is not a good catalyst for the high temperature hydrogenation of water soluble bio-oil components because it produces large amounts of light alkanes (primarily methane).

Table 5, Product yield and selectivity over 5 wt% RuC catalyst in single stage (T: 125°C, P: 750 psi; WHSV: 3 hr⁻¹) and 2-stage (P: 750 psi; WHSV: 3 hr⁻¹) hydrogenation of WSBO. * WHSV: 6 hr⁻¹.

Products distribution	Carbon yield, %				
	1-stage	200°C	220°C	250°C*	250°C
C₁-C₄ Alkanes & other gases	7.5	25.0	28.6	61.7	19.1
Gasoline cut 1 (boiling range: 60-100 °C)	2	6.1	5.5	11.9	4.8
Gasoline cut 2 (boiling range: 115-160 °C)	6.3	5.0	5.5	7.8	5.0
C₂-C₆ Diols	21.1	11.5	14.2	3.6	15.8
Lactones	3	1.1	2.4	0.4	2.4
Acetic acid	5.2	4.2	4.2	1.1	4.4
Sorbitol	10	9.4	4.1	0.0	6.4
Other chemicals	10.7	3.2	5.4	3.0	5.8
Unidentified	34.3	34.5	30.2	10.4	36.4

As shown in Figure 5A, the gasoline-cuts and diols production is maximised at 250 °C and 750 psi (40%). Also, the acid concentration decreases from about 6% from the 1-stage to less than 2% using the 2-stage ruthenium followed by platinum catalysts at 250 °C. However, a large fraction of carbon (28%) is lost to gas at higher temperatures (250 °C-750 psi). This can be reduced by operating the reactors at higher pressure (See Figure 5B).

The amount of hydrogen consumption decreases with increasing pressure. We estimate that the APP process over Ru/C at 250 °C and 750 psi requires about 7 wt% of H₂, while the APP process at the same temperature but higher pressure (1445 psi) requires only 4 wt% of hydrogen. This is 1 fold lower H₂ consumption than a 2-stage hydrotreating of bio-oil compounds over sulfided CoMo catalyst [35].

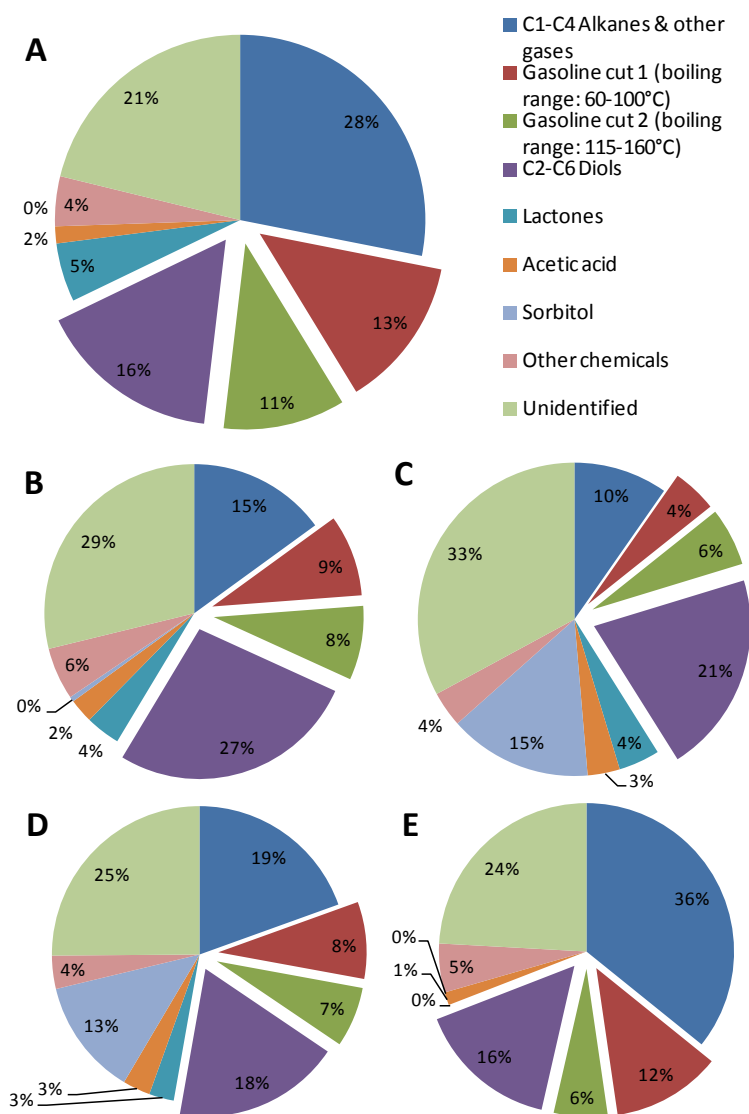


Figure 5 Product selectivity in single and 2-stage hydrogenation of aqueous fraction of bio-oil A: Ru/C-Pt/C, 125-250 °C, 750 psi, B: Ru/C-Pt/C, 125-250 °C, 1450 psi, C: Ru/C-Pt/C, 125-220 °C, 1450 psi, D: Ru/C-Pt/C, 125-220 °C, 750 psi, E: Ru/C-Pt/C, 125-275 °C, 1450 psi.

3.3 Hydrogenation reaction chemistry

Figure 6 depicts the reactions pathways identified in the low temperature hydrogenation (LTH) and high temperature hydrogenation (HTH) reactions. Four key classes of reactions have been identified: (1) primary hydrogenation of carbonyl groups at low temperature (H_2) to corresponding alcohols, (2) hydrolysis of levoglucosan C-O-C bonds to glucose in presence of acid sites (C-O-C cleavage), (3) hydrogenolysis reactions of polyols such as sorbitol with C-C bond cleavage (C-C cleavage), and (4) secondary hydrogenation reactions in presence of metals (C-O cleavage) where monohydric alcohols are produced from diols.

In the 1st group of reactions, hydroxyacetaldehyde is converted to ethylene glycol and hydroxyacetone to propylene glycol. About 90% of 5-HMF is converted to γ -hydroxymethyl- γ -valerolactone and furfural is hydrogenated to furfuryl-alcohol. Furfuryl alcohol is further hydrogenated into tetrahydrofurfuryl alcohol. Guaiacol methoxy functional groups ($-OCH_3$) are hydrogenated to $-OH$ groups. Then, catechol and phenol undergo cyclic hydrogenation of their C=C bonds, leading to saturation of their aromatic rings into cyclohexanol and 1,2-cyclohexanediol. The hydrogenation mechanism of aromatic rings differs from the direct hydrogenolysis of the hydroxy-groups when sulphides catalysts are used [16,22]. The hydrogenation of 2(5H)furanone, the saturation of the aromatic rings and the hydrolysis/hydrogenation of levoglucosan (2nd group of reactions) only occur at low conversion in the LHT conditions used in this paper as shown in Table 2.

In the 3rd group of reactions, which are very prominent in the HTH step, the hydrogenolysis of the polyols formed in the LTH such as sorbitol undergo C-C bond cleavage reactions over metal catalytic sites producing smaller polyols such as EG and PG. Tetrahydrofurfuryl alcohol is further converted in tetrahydrofuran by C-C bond cleavage. Tetrahydrofuran can be further

converted into butanol by C-O-C bond cleavage under high temperature hydrogenation in presence of platinum.

Finally, the 4th reaction pathway is represented by secondary hydrogenation reactions (C-O bond cleavage reactions), which are present in LTH but are prominent in HTH. Mono-alcohols are formed by dehydration of diols and light hydrocarbons such as methane, ethane, propane and butane are generated by secondary hydrogenation of mono-alcohols. Methane can be also formed from CO and CO₂ hydrogenation, especially on Ru. In addition, further HDO of monohydric alcohols produces the corresponding alkanes. Acetic acid was not successfully hydrogenated to the corresponding alcohol at either the LTH or the combined LTH/HTH conditions used in this paper.

Overall, the number of reactions involved during the 2-step process was found to be much greater compared to those happening during the single stage process. In fact, a higher number of the products including linear polyols, linear diols and alkanes were detected from the 2 stage process. The WSBO conversion and products selectivity can be further improved by tuning the relative reactions pathways and designing catalysts more reactive in the WSBO hydrogenation. Cellulose hydro-treating in presence of bimetallic catalysts (metal-tungsten; Raney Ni and H₂WO₄) at higher conditions (870ppsi; 245°C, batch reactor) selectively converted 65-75 wt% of the feed into EG, denoting a strong activity on C-C bonds cleavage and intermediate compounds hydrogenation, which was controlled by the weight ratio of the metal species[36-37]. This is in agreement with cellobiose/levoglucosan hydrogenation of this work (50 wt% sorbitol in 1stage at 125°C and 750psi), which shows higher selectivity for EG and PG in the 2nd HTH stage due to C-C and C-O bonds cleavage higher activity.

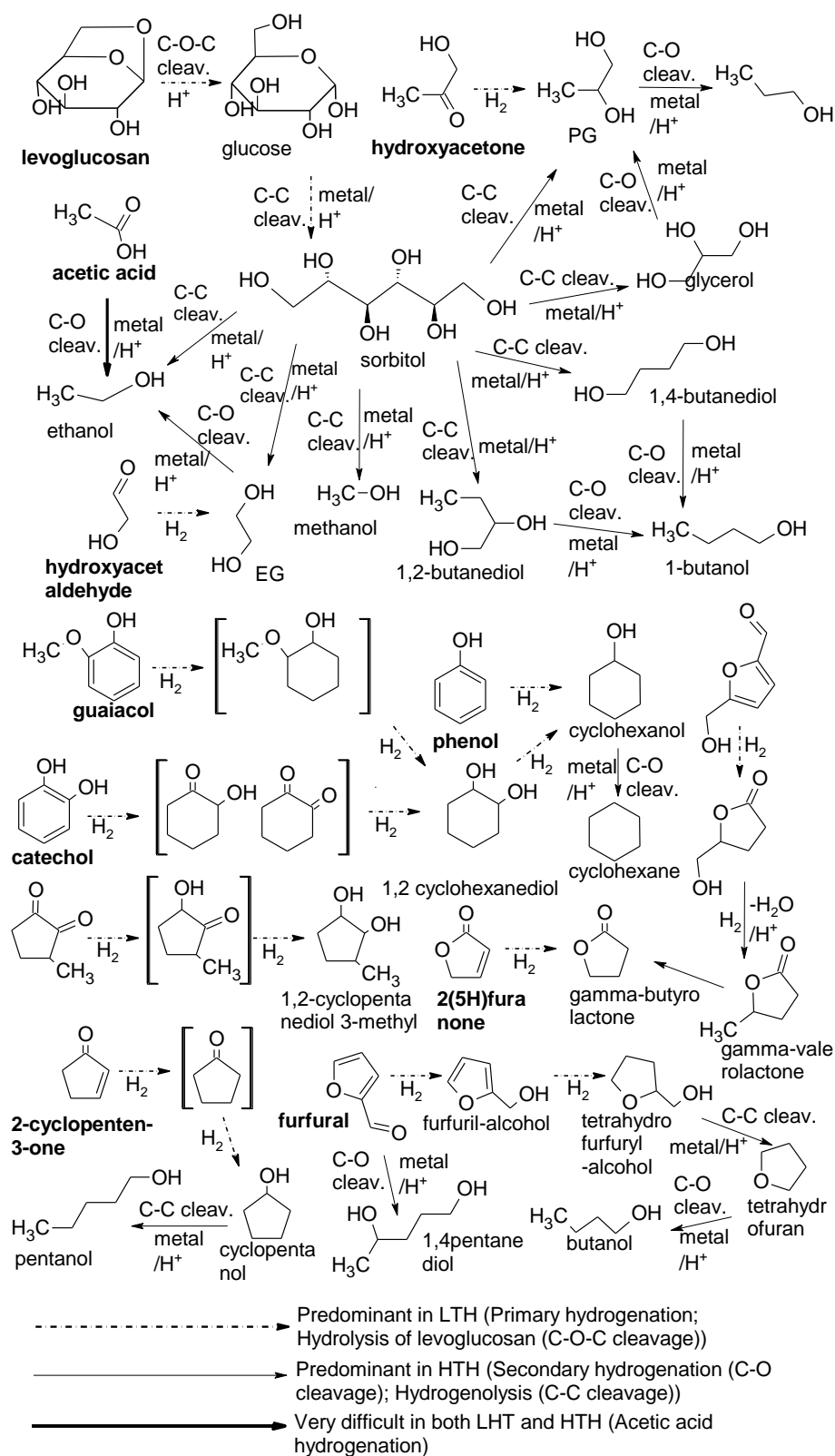


Figure 6 Reactions network involved in the conversion of bio-oil. Reactants' names in bold, [] intermediate compounds.

4.0 Summary

This study shows that oxygenated gasoline additives, alcohols, and diols can be produced from the aqueous fraction of the bio-oil in a 2-stage continuous hydrogenation process. The aqueous fraction of the bio-oil contains a wide range of C2 to C6 oxygenated compounds such as aldehydes, ketones, acids, and carbohydrates. These functionalities are thermally unstable; hence a direct high temperature hydrogenation of bio-oil or WSBO is not feasible. A LTH step converts the aldehydes, ketones, and sugars to their corresponding alcohols with a Ru catalyst. The alcohols are thermally stable and can be further converted in the desired products by HTH. Since ruthenium is highly active for the C-C bond cleavage reactions, the minimum possible temperature (125°C) to avoid homogeneous coke formation should be used in the low temperature hydrogenation step. LTH at temperatures above 125°C led to homogeneous coking reactions which plug the reactor. At this temperature, WSBO functionalities are able to hydrogenated with minimal (7%) carbon loss to gas and solid phase products. No signs of deactivation was observed in LTH after 80 hours' time on stream. The optimum space velocity was found to be 1.5-3 h⁻¹. Under these conditions the main hydrogenation products are EG, PG and sorbitol. Acetic acid is not hydrogenated in LTH. LTH products contain a large amount of sorbitol derived from the hydrogenation of levoglucosan and glucose. A HTH step was added to convert sorbitol to products including diols and monohydric alcohols. Hydrogenolysis (C-C bonds cleavage) and secondary hydrogenation reactions (C-O bonds cleavage) are predominant in the HTH step.

Platinum was found to be a suitable catalyst for HTH. Up to 45% carbon of the WSBO was successfully converted to gasoline blendstocks and C2 to C6 diols. The product distribution from the 2-stage hydrogenation can be controlled using the pressure and 2nd stage temperature. High

yields of gasoline blendstocks can be obtained by operating at low total pressure or at high second stage temperature (*e.g.* 275 °C). High pressure in the 2-stage process minimizes carbon loss to gas phase.

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Supplementary material

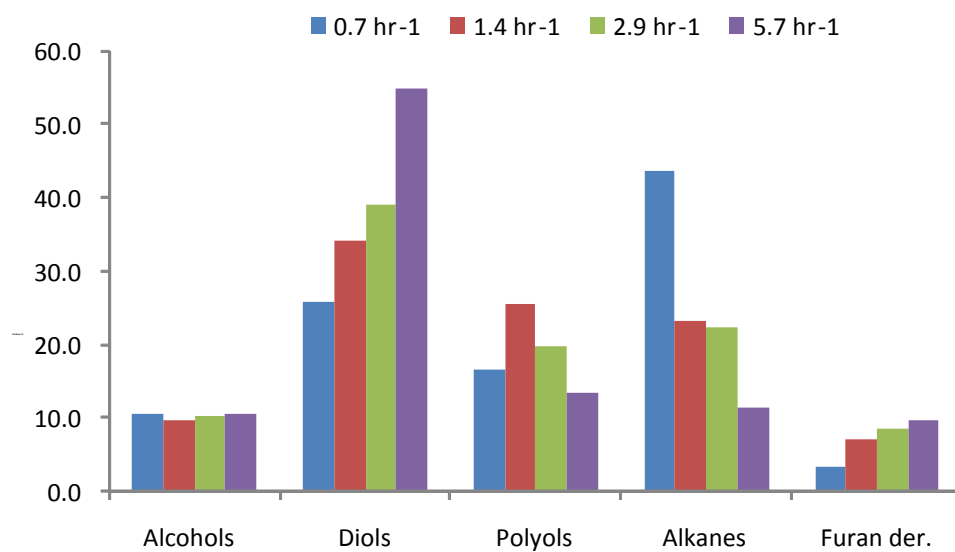


Figure A Carbon distribution (wt%) under different WHSV.